

## The role of thermally-induced internal stresses on the tunability of textured barium strontium titanate films

A. Sharma, Z.-G. Ban, and S. P. Alpay<sup>a)</sup>

*Department of Metallurgy and Materials Engineering and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269*

J. V. Mantese

*Delphi Research Laboratories, Shelby Township, Michigan 48315*

(Received 29 March 2004; accepted 11 June 2004)

The tunability of highly textured thin films of barium strontium titanate ( $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ , BST) is analyzed theoretically using a Landau–Devonshire thermodynamic model. The relative dielectric constant of BST films is determined as functions of the applied external electric field, deposition temperature, and the thermal expansion coefficient of the substrate. Our analysis shows that tunability is highly dependent upon thermally induced strains within the material. Both tension and compression produce deleterious tuning response. However, this effect can be minimized through judicious choices of deposition temperature and appropriate substrate material. © 2004 American Institute of Physics. [DOI: 10.1063/1.1781356]

In recent years much attention has been given to the development of tunable dielectric materials for voltage controlled phase shifters.<sup>1,2</sup> Such devices could have extensive use in both automotive and military steerable radar systems operating from X-band to millimeter wavelengths. The tunability (i.e., the degree of variation in the dielectric constant as a function of the applied electric field) is one of the key design parameters in paraelectric-based steerable microwave devices.<sup>3</sup> The choice of material systems for microwave device applications has primarily focused on perovskite oxides such as  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) and  $\text{SrTiO}_3$  (STO).<sup>4–9</sup> Current experimental efforts for improving the tunability and decreasing the dielectric loss of perovskite materials are often based upon a “cut and try” approach, adopted principally because of the lack of a fundamental theoretical formalism with capabilities for predicting the net properties of the underlying paraelectric materials and guiding the deposition process. Such a theory would be beneficial in rapidly developing the optimized materials necessary for steerable antenna systems.

Recent experimental studies have shown that internal stresses have a great impact on the dielectric behavior of BST thin films.<sup>10–12</sup> Significant variations in the dielectric constant (close to an order of magnitude) have been observed in epitaxial BST thin films for which the internal stress levels were systematically altered either by using different substrate materials or by adjusting the film thickness. Experimental results also indicate that the tunability of BST films displays strong dependence on the lattice misfit, or the misfit strain. For example, it was shown that annealing treatments to reduce residual stresses in  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$  films could improve the tunability from 36% to 52% for a 57 kV/cm field on a “compressive”  $\text{LaAlO}_3$  substrate (i.e., substrate with lattice parameters smaller than the film such that compressive stresses are induced in the plane of the film–substrate interface in pseudomorphic films) but reduce the tunability from 47% to 38% on a “tensile”  $\text{MgO}$  substrate.<sup>5</sup> An increase in

the tunability from 20% to 32% for a 40 kV/cm field was reported for  $\text{Ba}_{0.35}\text{Sr}_{0.65}\text{TiO}_3$  films on  $\text{LaAlO}_3$  substrates after an annealing treatment.<sup>11</sup>

In a recent publication, we have analyzed the effect of epitaxial strains on the tunability of BST films<sup>13</sup> considering the possibility of the formation of “unusual” phases that cannot form in bulk BST ceramics or single crystals by using a Landau–Devonshire phenomenology.<sup>14</sup> In this letter, we employ a similar treatment to analyze the tunability of highly textured BST films. Our goal is to provide a quantitative estimation for the dependence of the tunability on thermally induced internal stresses.

Consider a (001)-textured polycrystalline perovskite ferroelectric film that undergoes a cubic ( $Pm\bar{3}m$ ) to tetragonal ( $P4mm$ ) phase transformation upon cooling, deposited in the paraelectric state between two electrodes on a thick substrate (Fig. 1). A Cartesian coordinate system is defined with  $x_1 \parallel [100]$ ,  $x_2 \parallel [010]$ , and  $x_3 \parallel [001]$  as shown in Fig. 1. We assume that the grain size  $D$  is comparable to the film thickness  $h$ . The spontaneous polarization of the ferroelectric is oriented parallel to the  $z$  axis such that  $P = P_3$  and  $P_1 = P_2 = 0$ , a reasonable assumption for very small deviations of the spontaneous polarization direction for highly (001) textured films. Since films are usually deposited at elevated temperatures, there are internal stresses that develop in the film due to difference in thermal expansion coefficient (TEC) of the film and the substrate. The thermal stresses give rise to a

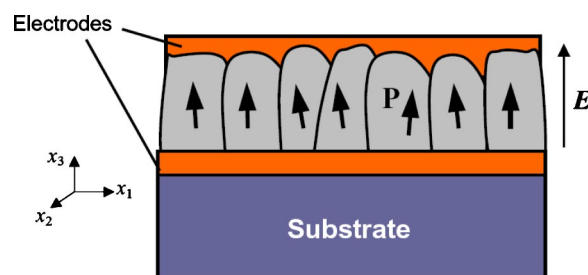


FIG. 1. (Color online) Schematic diagram of (001) textured polycrystalline ferroelectric thin film grown on a single crystal cubic substrate.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: p.alpay@ims.uconn.edu

biaxial strain state in the  $x_1$ - $x_2$  plane such that the in-plane strains are  $u_1 = u_2 = u_T$ , where  $u_T = (\alpha_F - \alpha_S) \Delta T$ ,  $\alpha_F$  and  $\alpha_S$  are the TECs of the film and the substrate, respectively, and  $\Delta T$  is the difference between deposition temperature  $T_G$  and RT (room temperature, 25 °C). All tensor quantities are given in contracted notation. Taking into account the mechanical boundary conditions, i.e., no shear stresses ( $\sigma_4 = \sigma_3 = \sigma_6 = 0$ ) and no out-of-plane stress ( $\sigma_3 = 0$ ), the free energy per unit volume of the film can be expressed as<sup>15</sup>

$$G(P, T, u_T, E) = \bar{a}P^2 + \bar{b}P^4 + cP^6 + \frac{u_T^2}{S_{11} + S_{12}} - EP, \quad (1)$$

where  $P$  is the polarization, and  $E(\parallel x_3)$  is the applied electric field. For a film under biaxial stress, the renormalized expansion coefficients of the free energy functional are given as

$$\bar{a} = a - u_T \frac{2Q_{12}}{S_{11} + S_{12}}, \quad \bar{b} = b + \frac{Q_{12}^2}{S_{11} + S_{12}}, \quad (2)$$

where  $a$  is the dielectric stiffness,  $b$  and  $c$  are higher order stiffness coefficients at constant stress,  $Q_{12}$  is the electrostrictive coefficient, and  $S_{11}$  and  $S_{12}$  are the elastic compliances of the film at constant polarization. The temperature dependence of the dielectric stiffness  $a$  is given by the Curie-Weiss law,  $a = (T - T_C) / 2\epsilon_0 C$ , where  $C$  is the Curie-Weiss constant of a bulk ferroelectric, and  $\epsilon_0$  is the permittivity of free space.

In the presence of applied electric field  $E$ , the dielectric constant along the direction of the applied field is given by

$$\epsilon(E) = \left( \frac{\partial^2 G}{\partial P^2} \right)^{-1} = \frac{1}{2(\bar{a} + 6\bar{b}P^2 + 15cP^4)}, \quad (3)$$

where  $P$  is obtained by solving the equation of the state:

$$\frac{\partial G}{\partial P} = 2\bar{a}P + 4\bar{b}P^3 + 6cP^5 - E = 0. \quad (4)$$

The tunability can be defined as the ratio of the variation of the dielectric constant at a given electric field  $E$  to the dielectric constant at zero bias:

$$\varphi = \frac{\epsilon(E=0) - \epsilon(E)}{\epsilon(E=0)}. \quad (5)$$

Since the internal stresses in polycrystalline or textured films are predominantly due to thermal stresses, the growth temperature and the TECs of substrates and films are expected to have substantial effects on the tunability. In Fig. 2 we plot the theoretically calculated tunability of (001) textured polycrystalline BST 50/50 thin film on substrates having a variety of TECs (in units of  $10^{-6} \text{ }^\circ\text{C}^{-1}$ ) as a function of growth temperature  $T_G$ . The film is assumed to be under an applied bias,  $E = 50 \text{ kV/cm}$ . The thermodynamic parameters, elastic, and electrostrictive constants for the BST 50/50 film are obtained by averaging the corresponding single-crystal parameters of  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$ .<sup>16</sup> Considering that the TEC of BST 50/50 is  $10.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  and  $u_T = (\alpha_F - \alpha_S) \Delta T$ , Fig. 2(a) plots the tunability of BST 50/50 on “tensile” substrates (substrates with TEC smaller than the film such that tensile in-plane stresses are developed in the film as it cools down from growth temperature) while Fig. 2(b) shows the tunability of film on “compressive” substrates.

Figures 2(a) and 2(b) reveal that regardless of whether the substrate is tensile or compressive, higher growth tem-

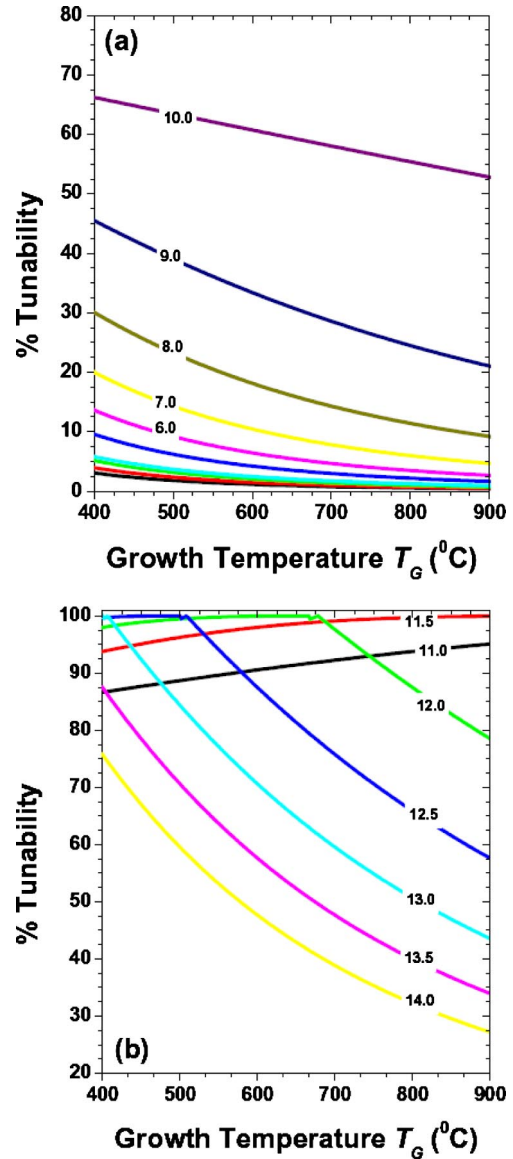


FIG. 2. (Color online) Calculated tunability of (001) textured polycrystalline  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  thin films as a function of the deposition temperature on substrates exerting (a) tensile and (b) compressive thermal internal stresses on the film. Applied bias  $E = 50 \text{ kV/cm}$ . Each curve is labeled with the thermal expansion coefficient of the substrate in the unit of  $10^{-6} \text{ }^\circ\text{C}^{-1}$ .

peratures result in larger thermal stresses and thus smaller tunability. This effect is more remarkable for compressive substrates for which there may be significant decrease in the tunability for films deposited at elevated temperatures. It is interesting to note that for compressive substrates with TECs equal to 11 and  $11.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , a slight loss in tunability is predicted if the growth temperature is lowered.

Figures 2(a) and 2(b) also show that high levels of thermal stresses and low tunability are expected for substrates with large differences in TECs compared to BST ( $10.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ). For films deposited on tensile substrates, the tunability increases with a decrease in tensile stress as the TEC of the substrate approaches that of the film where maximum tunability is predicted as observed in Fig. 2(a). For films deposited on compressive substrates, tunability is maximized when the substrate has TEC close to that of the film, and it decreases with further decrease in the TEC of the substrate when the TEC of substrate is in the range of 11.5 to  $11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

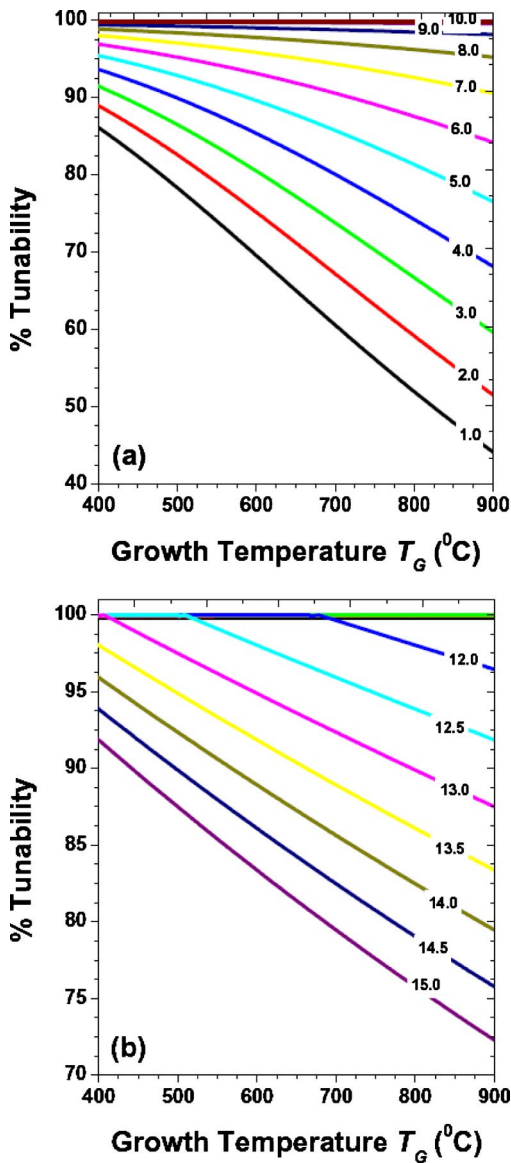


FIG. 3. (Color online) Calculated tunability of (001) textured polycrystalline  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  thin films as a function of deposition temperature on substrates exerting (a) tensile and (b) compressive thermal internal stresses on the film. Applied bias  $E=700$  kV/cm. Each curve is labeled with the thermal expansion coefficient of the substrate in the unit of  $10^{-6} \text{ }^\circ\text{C}^{-1}$ .

The general features of Figs. 2(a) and 2(b) as discussed earlier are due to thermal stresses that can be controlled by appropriate selection of a deposition temperature and a substrate material. The analysis indicates that the tunability peaks at a critical small compressive strain  $u_T^0$  ( $\sim -0.1\%$ ) corresponding to a phase transformation from the paraelectric phase to the ferroelectric phase induced by the thermal stresses. This strain can be determined by setting  $\bar{a}=0$  in Eq. (2) such that

$$u_T^0 = \frac{S_{11} + S_{12}}{4\varepsilon_0 C Q_{12}} (T - T_C). \quad (6)$$

The tunability drops off for either a decrease or increase in the strain away from this critical value (see also Fig. 6 of Ref. 13).

Obviously, the tunability reflects the variation of the dielectric permittivity with applied bias as given in Eq. (5). Consequently, the tunability depends upon the magnitude of

the applied bias and it increases with increasing the electric field. Figures 3(a) and 3(b) present the respective counterparts of Figs. 2(a) and 2(b), but with an applied electric field  $E=700$  kV/cm. It can be seen from Figs. 3(a) and 3(b) that at such high fields, there is a substantial enhancement in tunability for both compressive and tensile substrates. Even for tensile substrate with a TEC around  $1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , a reasonably good tunability  $\sim 45\%$  at  $T_G=900$  °C is predicted. These results indicate that a ferroelectric thin film with a high breakdown field is desirable in order to achieve substantial enhancement in tunability at large applied bias.

The calculated tunability is compared with published experimental results. A tunable response of  $\sim 75\%$  [Fig. 3(a)] is predicted for TEC  $\sim 2$  to  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , which is close to the TEC of Si (bulk value varies from  $2.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  at 25 °C to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  at 850 °C), and agrees with the experimentally reported values by Jaemo *et al.*<sup>17</sup> The calculated tunability on MgO (TEC  $13.47 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) is consistent with the experimentally reported value of 47% [Fig. 2(b)] for a BST deposition temperature of 750 °C.<sup>5</sup>

In conclusion, we have analyzed the dependence of the tunability on thermally induced internal stresses in highly textured BST films via a Landau–Devonshire thermodynamic model. Our model does not rely upon any adjustable parameters, and being simple, can be applied to any film–substrate system. It has been shown that choice of the deposition temperature and the thermal expansion coefficient of the substrate can be used as design parameters to achieve desirable tunability of ferroelectric thin films.

The work at UConn was supported by NSF under Grant No. DMR-0132918.

<sup>1</sup>C. H. Mueller and F. A. Miranda, in *Handbook of Thin Film Devices*, edited by D.J. Taylor and M.H. Francombe (Academic, San Diego, 2000), p. 113.

<sup>2</sup>A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh, and N. Setter, *J. Electroceram.* **11**, 5 (2003).

<sup>3</sup>M. W. Cole, W. D. Nothwang, C. Hubbard, E. Ngo, and M. Ervin, *J. Appl. Phys.* **93**, 9218 (2003).

<sup>4</sup>J. Im, O. Auciello, and S. K. Streiffer, *Thin Solid Films* **413**, 243 (2002).

<sup>5</sup>C. M. Carlson, T. V. Rivikun, P. A. Parilla, J. D. Perkins, D. S. Ginley, A. B. Kozыrev, V. N. Oshadchy, and A. S. Pavlov, *Appl. Phys. Lett.* **76**, 1920 (2000).

<sup>6</sup>C. L. Chen, J. Shen, S. Y. Chen, G. P. Luo, C. W. Chu, F. A. Miranda, F. W. Van Keuls, J. C. Jiang, E. I. Meletis, and H. Y. Chang, *Appl. Phys. Lett.* **78**, 652 (2001).

<sup>7</sup>P. Padmini, T. R. Taylor, M. J. Lefevre, A. S. Nagra, R. A. York, and J. S. Speck, *Appl. Phys. Lett.* **75**, 3186 (1999).

<sup>8</sup>H. C. Li, W. D. Si, A. D. West, and X. X. Xi, *Appl. Phys. Lett.* **73**, 190 (1998).

<sup>9</sup>A. R. James and X. X. Xi, *J. Appl. Phys.* **92**, 6149 (2002).

<sup>10</sup>W. Chang, C. M. Gilmore, W.-J. Kim, J. M. Pond, S. W. Kirchoefer, S. B. Qadri, D. B. Chrisey, and J. S. Horwitz, *J. Appl. Phys.* **87**, 3044 (2000).

<sup>11</sup>L. A. Knauss, J. M. Pond, J. S. Horwitz, D. B. Chrisey, C. H. Mueller, and R. Treece, *Appl. Phys. Lett.* **69**, 25 (1996).

<sup>12</sup>H. Li, A. L. Roytburd, S. P. Alpay, T. D. Tran, L. Salamanca-Riba, and R. Ramesh, *Appl. Phys. Lett.* **78**, 2354 (2001).

<sup>13</sup>Z.-G. Ban and S. P. Alpay, *J. Appl. Phys.* **93**, 504 (2003).

<sup>14</sup>N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).

<sup>15</sup>A. Sharma, Z. G. Ban, S. P. Alpay, and J. V. Mantese, *J. Appl. Phys.* **95**, 3618 (2004).

<sup>16</sup>The parameters used for the calculation of Figs. 2 and 3 are (in SI units,  $T$  in °C):  $\bar{a}=4.99 \times 10^5(T+23)+2.31 \times 10^{10}u_T$ ,  $\bar{b}=1.87T+10.79 \times 10^8$ . The sixth-order coefficient  $c$  is ignored in the calculations. Data compiled from Ref. 15.

<sup>17</sup>I. Jaemo, O. Auciello, P. K. Baumann, S. K. Streiffer, D. Y. Kaufman, and A. R. Krauss, *Appl. Phys. Lett.* **76**, 625 (2000).